Power for the Real World

2008 DOE Hydrogen Program Review

Advanced Cathode Catalysts and Supports for PEM Fuel Cells

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3M Company

June 10, 2008

Powered by 3M

Project ID FC 1

DOE Hydrogen Program

Overview

Timeline

- Project start : April 1, 2007
- Project end : March 30, 2011
- 30% Complete

Budget

- Total Project funding **$10.43MM**
  - $8.34 MM DOE and FFRDC
  - $2.09 MM 3M share
- Received in FY07: $0.565 Million
- Received in FY08: $0.711 Million through 3/08/08

Partners

- Dalhousie University (J. Dahn)
- JPL (S. R. Narayanan)
- ANL (N. Markovic)
- Project Management – 3M

Barriers

A. Electrode and MEA Durability
B. Stack Material & Mfg Cost
C. Electrode and MEA Performance

DOE Technical Targets

Electrocatalyst/ MEA		2010	2015
Lifetime Hrs, > 80°C		2000	5000
Mass Activity(A/mg)		0.44	0.44
PGM, (g/KW rated)		0.3	0.2
Performance	@ Rated	1	1
(W/cm^2)	@ 0.8V	0.25	0.25

Additional Interactions

LANL(NIST), ORNL(TEM), ANL(modeling), BASF(Pt recycling), Vendors (GDM/PEM), System Integrators

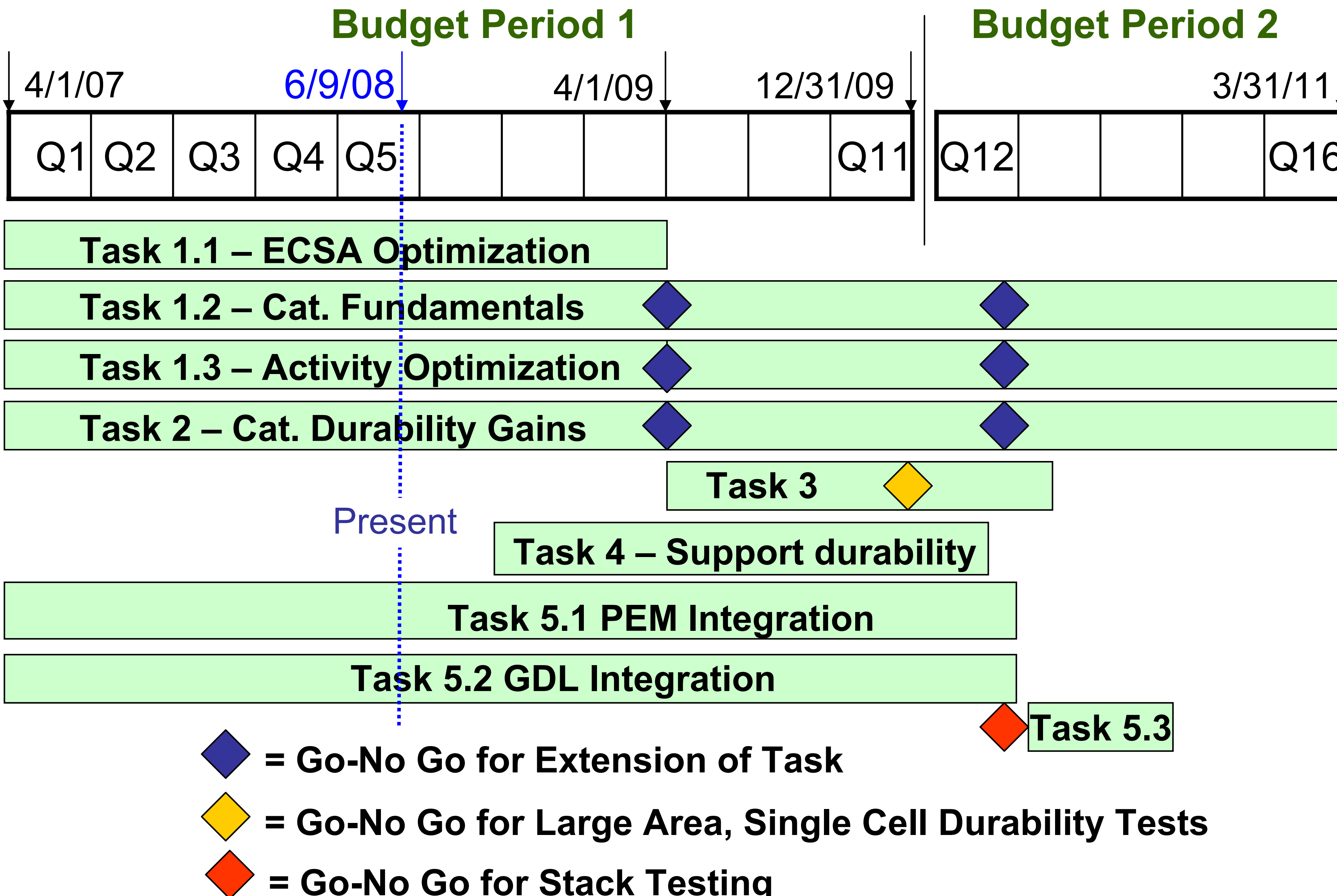
Overall Project Objectives

Development of a durable, low cost, high performance cathode electrode (catalyst and support), that is fully integrated into a fuel cell membrane electrode assembly with gas diffusion media, fabricated by high volume capable processes, and is able to meet the 2015 DOE targets.

Objectives for Past Year

- Apply DOE specified accelerated durability tests to benchmark the NSTF catalyst
- Define and implement multiple strategies for increasing catalyst surface area, activity, and durability with catalyst loadings of $\leq$ 0.25 mg-Pt/cm^2 total per MEA
- Work closely with collaborators to fabricate and screen new electrocatalysts using high throughput characterization methods, for durability and activity gains
- Conduct fundamental studies of the NSTF catalyst activities for ORR
- Define and implement multiple strategies to optimize the MEA water management
- Advance the high volume roll-good NSTF catalyst /membrane integration

Project Timeline and Milestones



Plan and Approach

Unique Aspect:

Development of advanced cathode catalysts and supports is based on 3M's nanostructured thin film (NSTF) catalyst technology platform.

Task 1.0 Catalyst Activity and Utilization Improvements

- 1.1 NSTF catalyst surface area increase and support optimization
- 1.2 Fundamentals of NSTF catalytic activity
- 1.3 New multi-element catalysts to increase activity

Task 2.0 Catalyst Durability Improvements

- 2.1 NSTF catalyst stabilization against dissolution
- 2.2 NSTF catalyst grain size stabilization

Task 3.0 Full Size (> 250 cm^2) Single Cell Performance and Durability Tests

Task 4.0 Durability Characterization of Advanced Support Structures

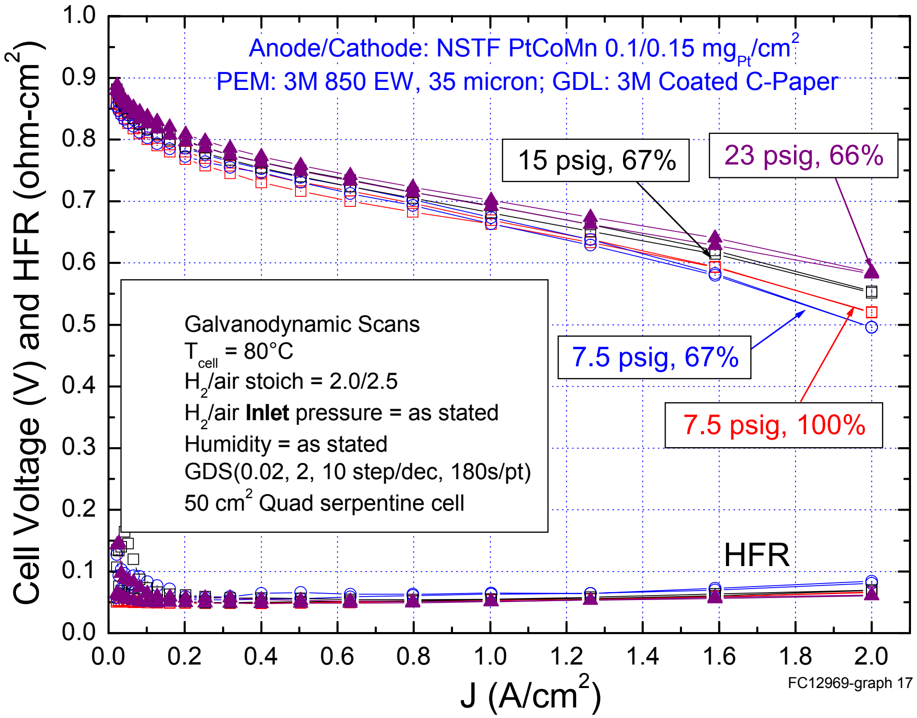
Task 5.0 Stack Testing and Optimized NSTF MEA Roll-good

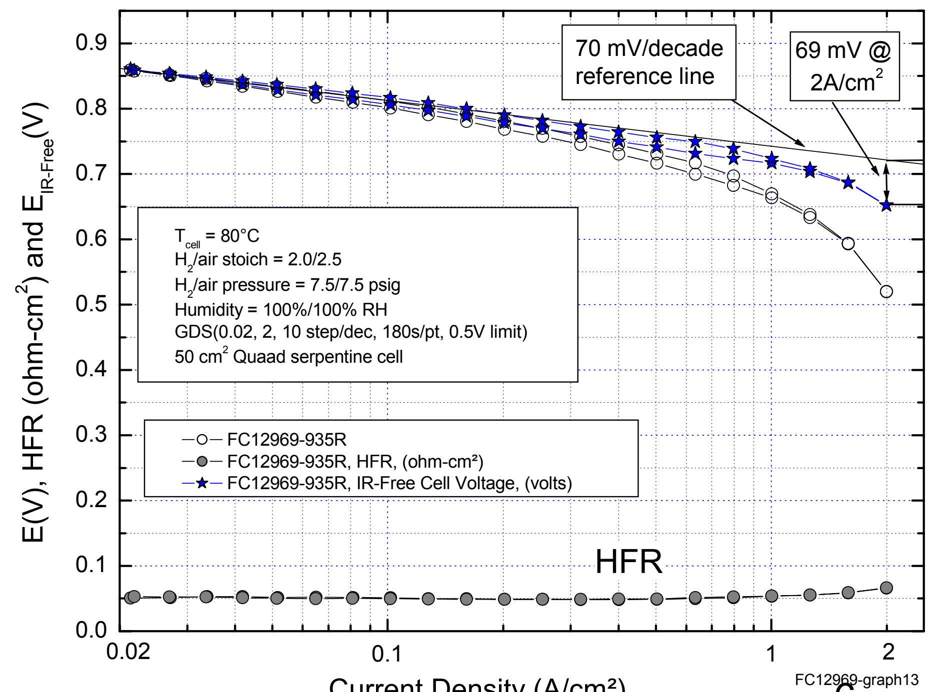
- 5.1 NSTF catalyst / low EW membrane interface optimization
- 5.2 Optimized anode and cathode GDL's
- 5.3 Short stack testing (> 10 cells, 312 cm^2)

= Underway

Technical Accomplishments: Improved catalyst roll-good fabrication and membrane integration

- Improved baseline performance of NSTF-PtCoMn with 0.25 mg-Pt/cm² total per MEA: **0.61 V at 1.5 A/cm² with 0.25 mgPt/cm² under 150kPa H_2/air inlet press. = 0.27g/kW**
- High current density improvements obtained by two factors:
  - reduced microstructured feature size of NSTF roll-good substrate
  - reduction of anode loading from 0.2 to 0.1 mg/cm² for better anode water transport and reduced HFR and iR-loss at 2 A/cm².

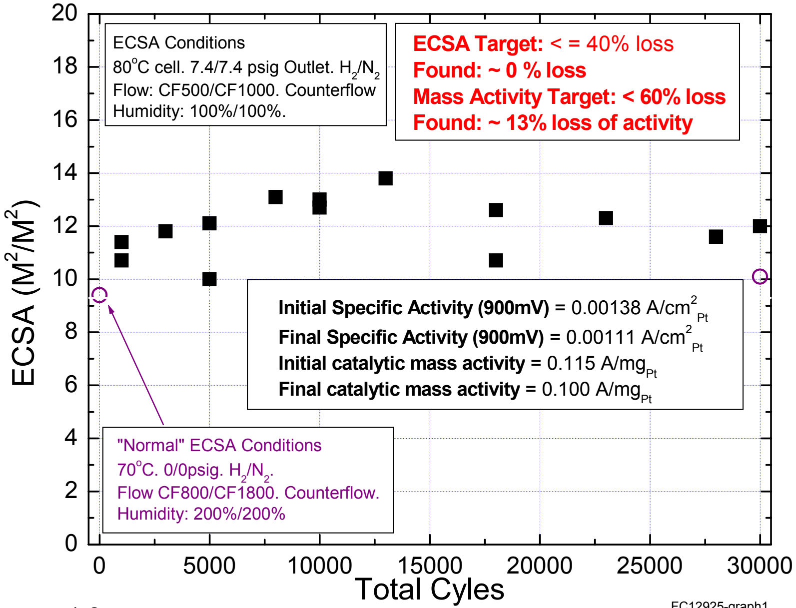




Technical Accomplishments: Accelerated Durability Test 1

3M

DOE Specified Protocol: 30,000 CV cycles, 0.7- 0.9 V step, 30 s hold, 80/80/80°C

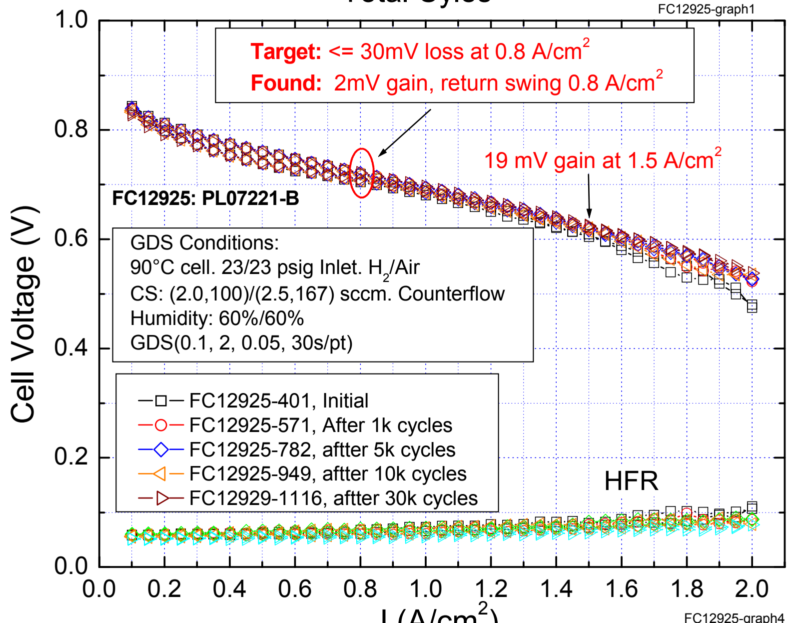


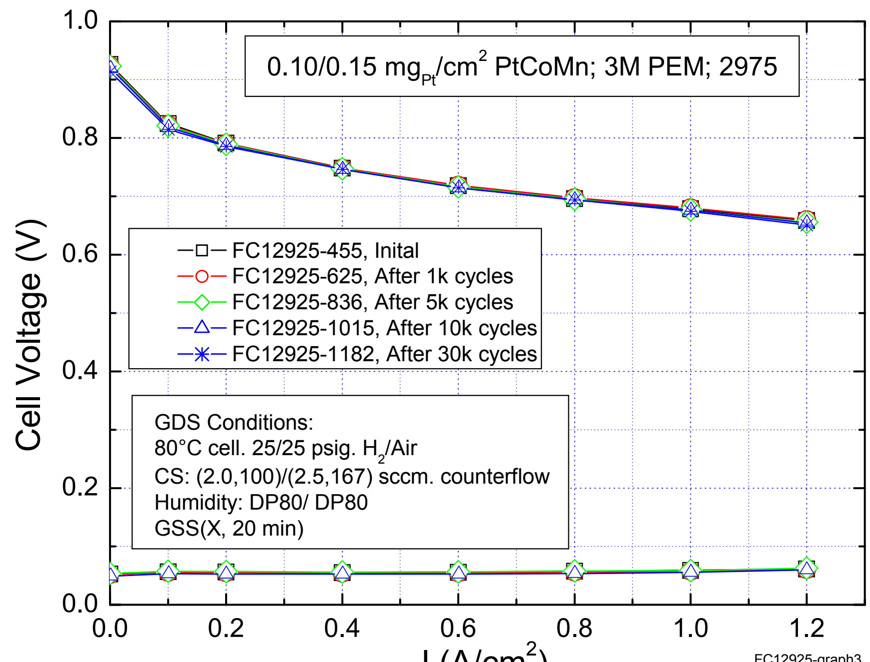
- Test evaluates Pt dissolution resistance
- Used NSTF PtCoMn: A/C 0.1/0.15 mg-Pt/cm^2
- ECSA loss target = 40%. Found ~ 0%.
- Mass activity loss target = < 60%. Found ~ 13%.
- Performance loss :

  Target = < 30mV loss at 0.8 A/cm^2

  Found 2 mV gain at 0.8 A/cm^2

  Found 19 mV gain at 1.5 A/cm^2.

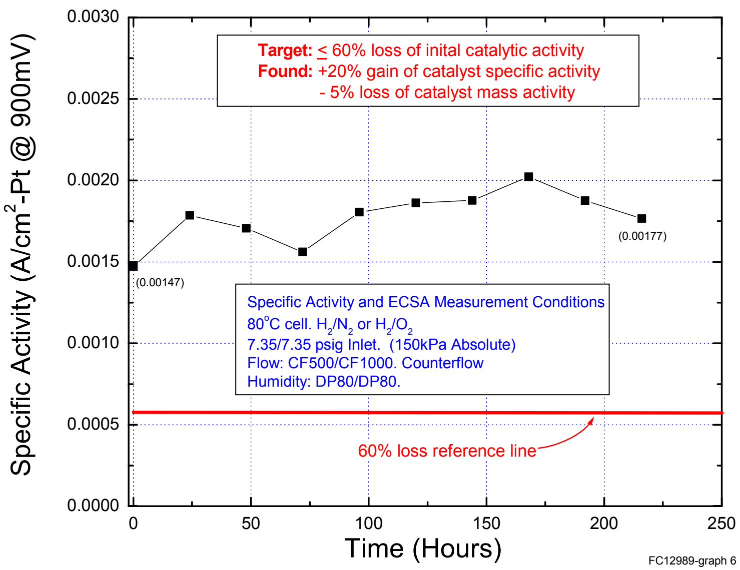




Technical Accomplishments: Accelerated Durability Test 2

3M

DOE Specified Protocol: 200 hour hold at 1.2 Volt and 95°C, H_2/N_2, 150kPa, 80%RH



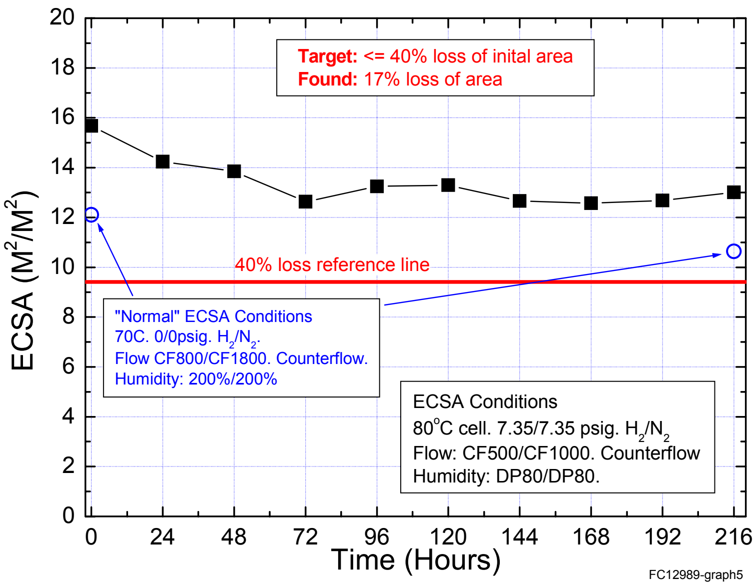
- Test evaluates support corrosion resistance
- Used NSTF PtCoMn: A/C 0.1/0.15 mg-Pt/cm^2
- ECSA loss target = 40%. Found ~ 16±1%, 2 trials
- Catalyst activity loss target = < 60%.

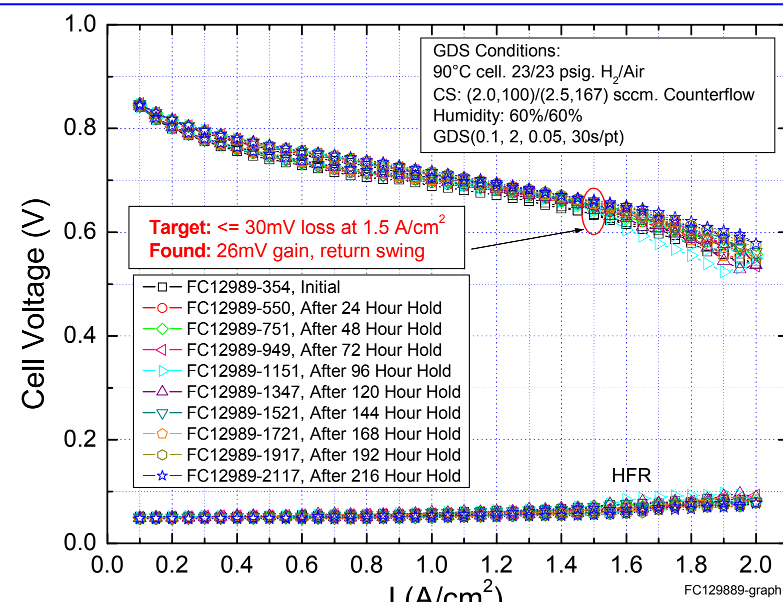
  Found 28% ± 7% gain in specific activity for 2 trials

  Found -5% /+15% loss/gain in mass activity, 2 trials
- Performance loss :

  Target = < 30mV at 1.5 A/cm^2

  Found 27 ± 1 mV gain at 1.5 A/cm^2, 2 trials

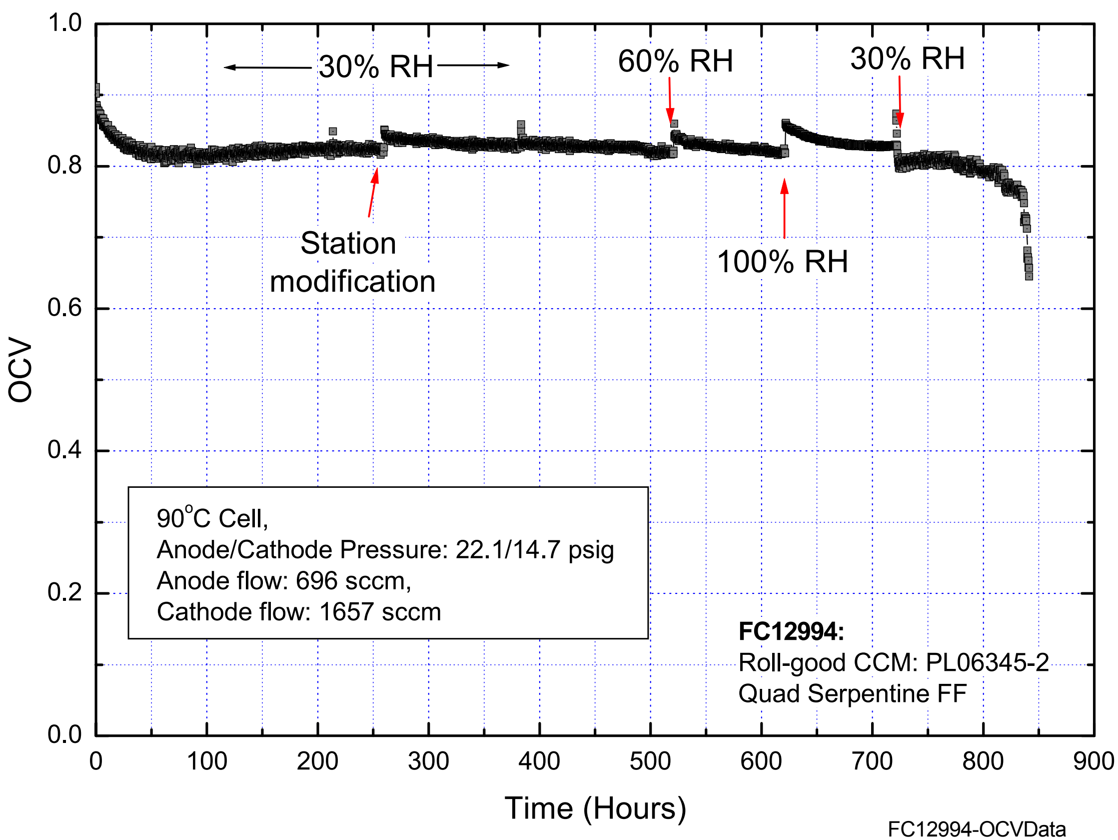




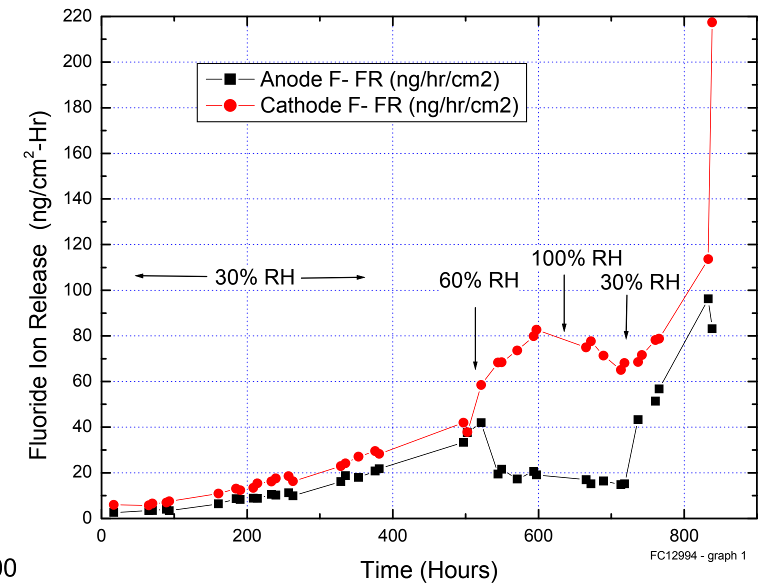
Technical Accomplishments: Accelerated Durability Test 3

DOE Protocol: 200 hour hold at OCV at 90°C under 250/200 kPa H_2/Air, 30% RH

- Test evaluates overall MEA chemical stability
- Used NSTF PtCoMn : A/C = 0.2 mg_{Pt}/cm^2
- 3M PEM, 850EW: not chemically stabilized and no MEA edge protection
- 200 hour lifetime target exceeded by factor of ~ 4.



F- ion release rate

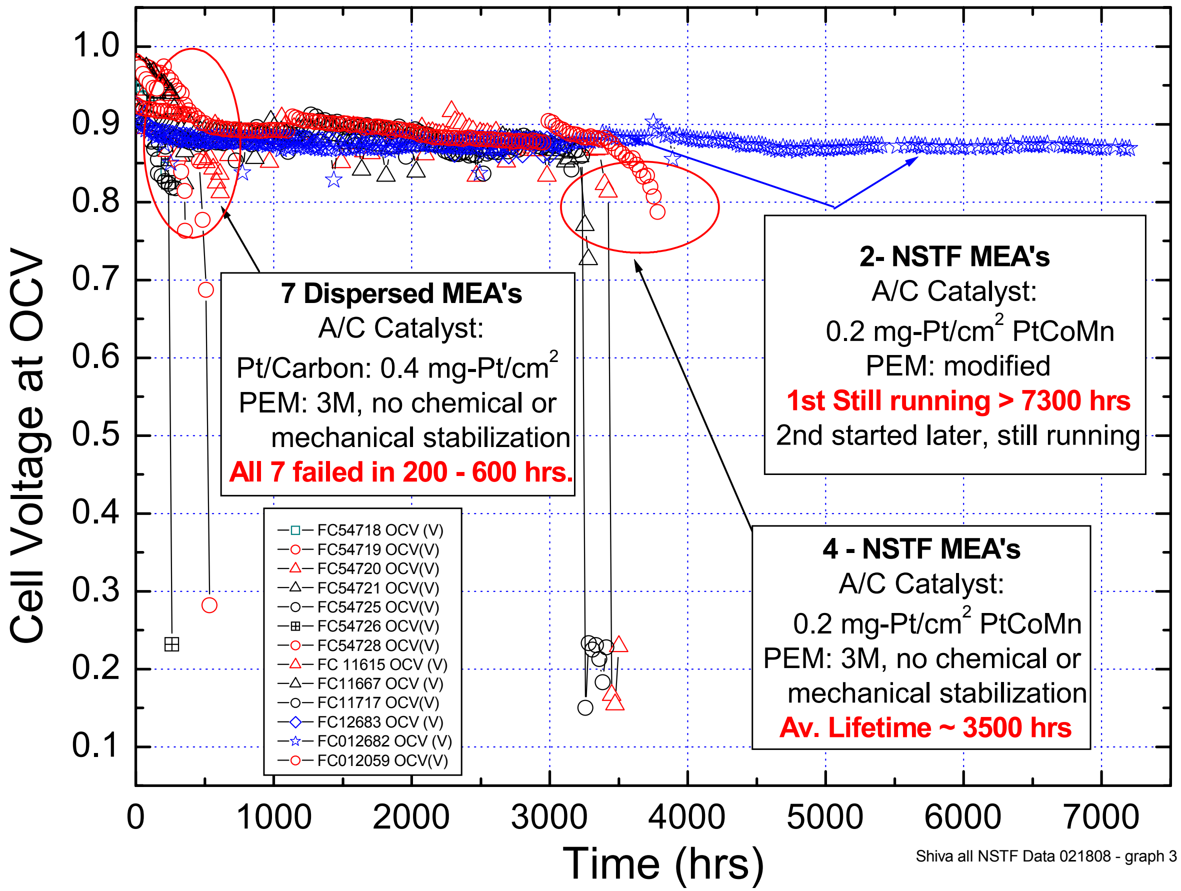


Technical Accomplishments: Accelerated Durability Test 4

3M

3M Specified Protocol: Accelerated lifetime load cycling with variable stoichiometry

- Tests MEA chemical stability due to catalyst influence. Correlates to F^- ion release rates.
- Previous contract: NSTF PtCoMn, A/C = 0.2 mgPt/cm^2 , on non-chemically stabilized 3M PEM demonstrated > 7x gain in lifetime to failure (defined as OCV < 0.8V) vs dispersed Pt/C.
- This project: used same NSTF catalyst and mechanically stabilized but neat 3M ionomer.
- First NSTF MEA's lifetimes exceeding 7300 hours and still running



Protocol at 80/64/64°C

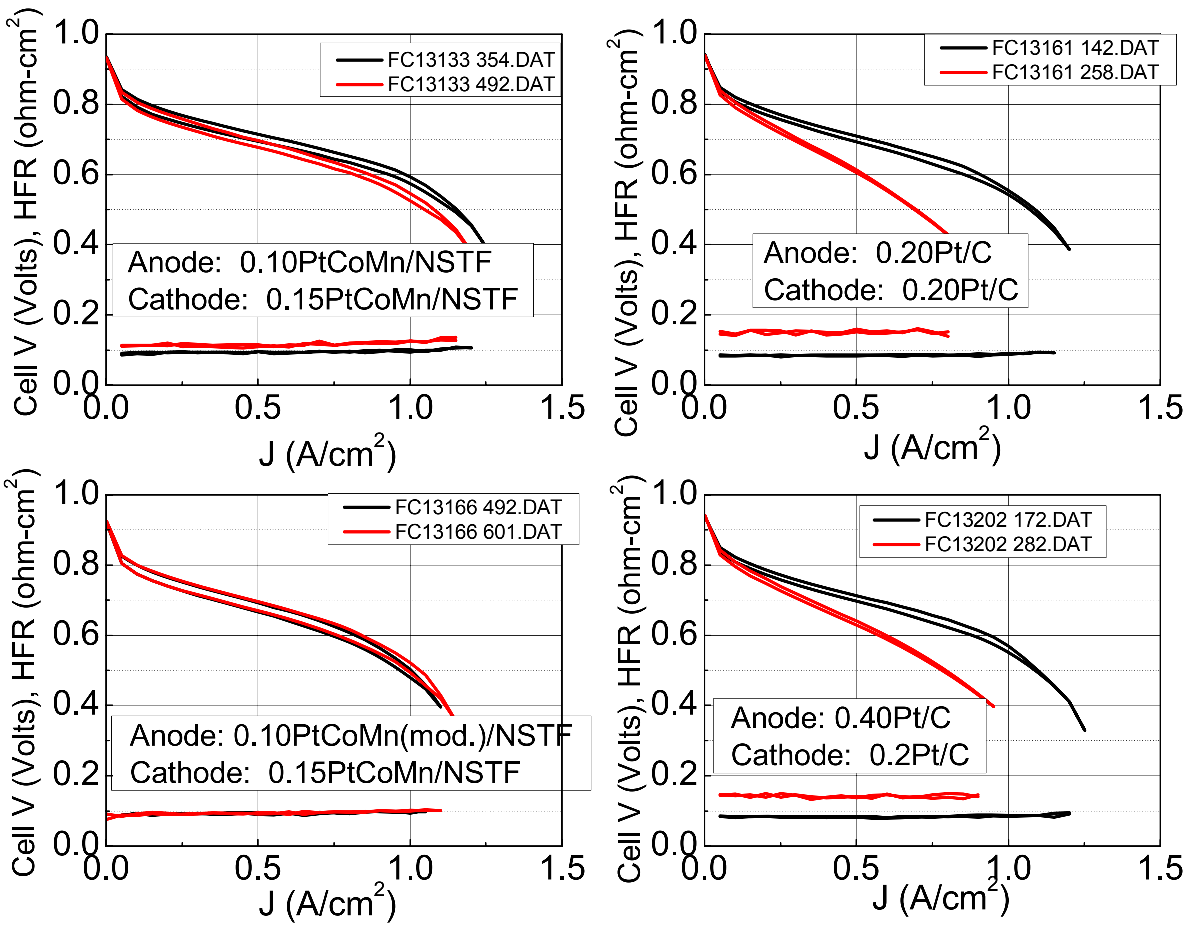
Test Point	J (A/cm^2)	Duration (min)	Stoich.
1	0.20	5	5
2	0.02	20	15
3	0.80	15	1.7
4	0.80	10	3
5	0.02	20	15
6	0.80	15	1.7
7	0.20	20	5
8	1.00	20	1.7

Technical Accomplishments: Accelerated Durability Test 5

3M Protocol: Anode forced to support 2 mA/cm^2 oxidation current for 5 hours under N_2.

- Tests anode resistance to corrosion under fuel starvation conditions.
- Graphs compare initial versus recovered performance of four types of MEA's
- Standard NSTF PtCoMn anode catalyst modified for improved oxygen evolution reaction

Anode Starvation Tolerance v. MEA Type



- The MEAs with dispersed Pt/C at 0.2 and 0.4 mg/cm^2 on the anode showed substantial decreases in performance and increased resistance that could not be recovered.
- The NSTF MEAs showed much less performance loss or increase in HFR.
- The modified NSTF anode catalyst showed even less loss of performance than the standard NSTF anode.
- Work continuing to try and optimize NSTF anode modification.

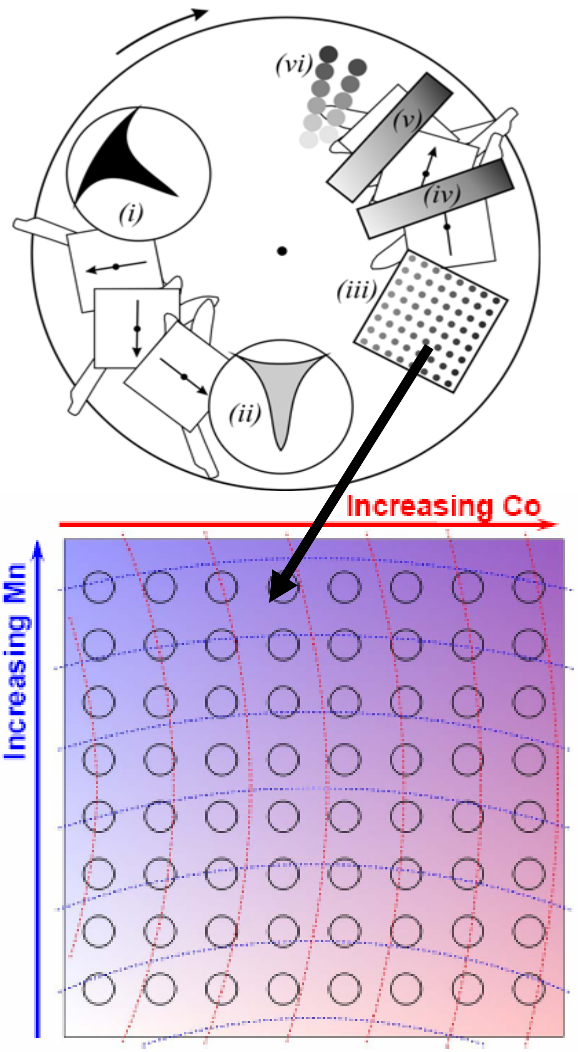
Technical Accomplishments: New NSTF catalysts

Prof. Jeff Dahn, David Stevens, Arnd Garsuch, and students

DALHOUSIE UNIVERSITY
Inspiring Minds

Advanced catalysts by compositional spread screening at Dalhousie University

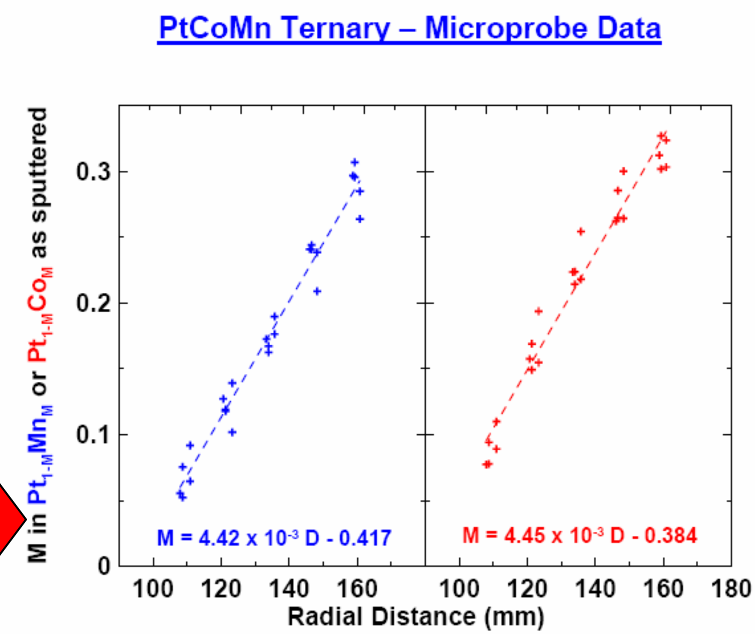
- 64-electrode arrays of thin film catalysts deposited onto NSTF whiskers, made into MEAs at 3M, tested at Dal.
- Over 60 libraries fabricated and tested to date
  - 25 different material sets combined in 5 distinct structural configurations.
  - Characterized for ECSA, ORR, high V durability, XRD, electron microprobe, acid soak resistance.



Circles show positions of fuel cell electrodes.

Dotted lines represent contours for constant Mn and Co respectively.

Example of composition control with PtCoMn

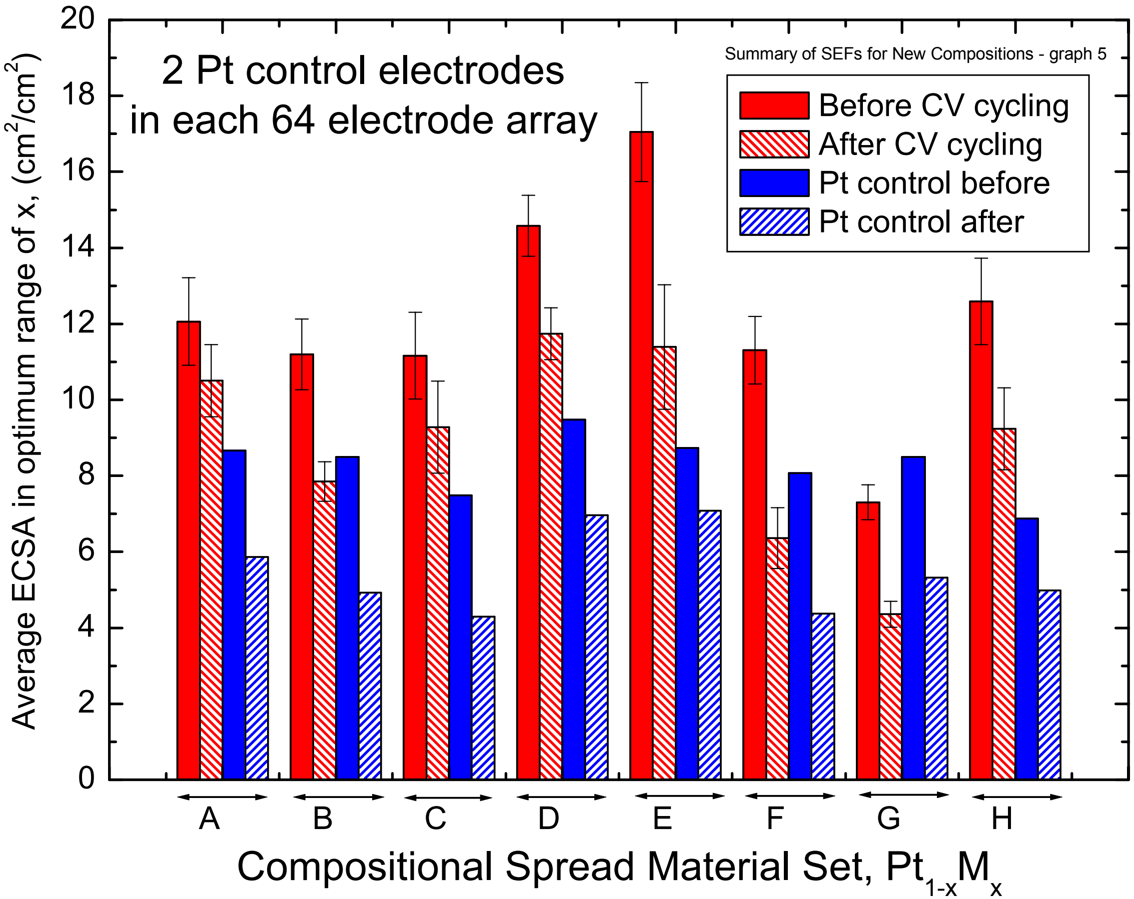


Technical Accomplishments: Dalhousie - continued

DALHOUSIE UNIVERSITY *Inspiring Minds*

Objective: Control grain size, lattice spacing, and surface composition to increase activity, catalyst surface area, stability under high voltage cycling,

Comparison of ECSA stability of eight different 64 electrode array compositional spreads before and after 3000 CV cycles from 0.6 – 1.2 V at 20mV/s under Ar vs 5% H_2 in Ar, at 75°C 100%RH, 500 sccm and no back-pressure. Pt controls are embedded in the arrays.



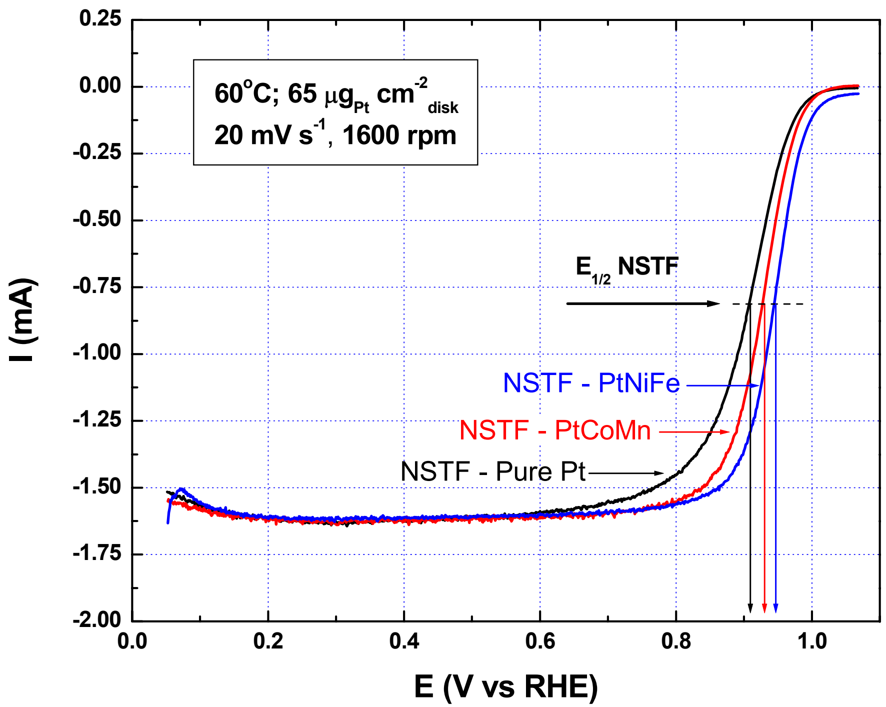
- Eight new catalyst material sets from one configuration found to have higher initial surface area compared to pure Pt controls.
- Most indicated surface area increases dependent on the mole fraction of the additive compound or element.
- Five indicated higher surface areas after 3000 CV cycles than the Pt controls had initially.

Technical Accomplishments - *ORR Activity and $E_{1/2}$ from RDE experiments*

V. Stamenkovic, Dennis van der Vliet, N. Markovic

Argonne NATIONAL LABORATORY

NSTF loading = (80 μg_{Pt} cm_{disc}^{-2})	i_{kin} at 0.875 V ($mAcm^{-2}$)	i_{kin} at 0.90 V ($mAcm^{-2}$)	i_{kin} at 0.925 V ($mAcm^{-2}$)	i_{kin} at 0.95 V vs RHE	$E_{1/2}$ (V)
Pt - NSTF	4.0	1.9	0.75	0.28	**0.92**
PtCoMn - NSTF	6.3	3.3	1.4	0.53	**0.94**
PtNiFe - NSTF	8.2	4.3	1.8	0.62	**0.95**
5nm **Pt / C** (> 100 μg_{Pt} cm_{disc}^{-2})	0.78	0.41	0.19	0.08	**0.91**



ORR on NSTF Surfaces by RDE

- High activity on all NSTF catalysts
- PtNiFe is the most active measured to date
- NSTF is 10x more active than Pt/C
- $E_{1/2}$: = 0.95 V (PtNiFe) vs. 0.91 V (Pt/C)
- Stable activity by CV and thermal cycling

CO Oxidation as a Probe of NSTF Activity

- The best activity on any Pt surface
- The onset of CO oxidation is at 0. 2 V
- Stable activity in narrow *E* range

Technical Accomplishments: New alloys for performance and durability gains.

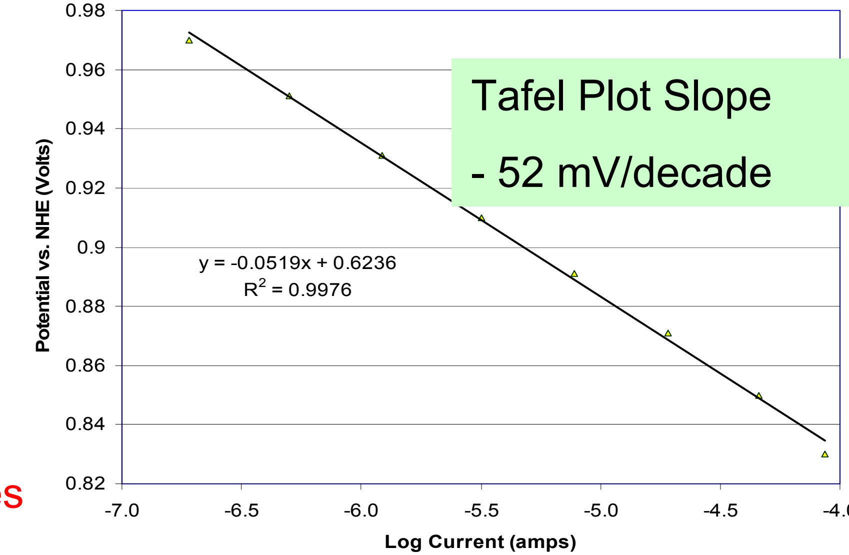
JPL: Charles C. Hays and S. R. Narayanan

Concept: Novel multi-electrode electrochemical cell with rotating electrolyte to simulate rotating disc electrode measurements. Apply sputtered alloys to 3M NSTF whisker supports in compositional spread.

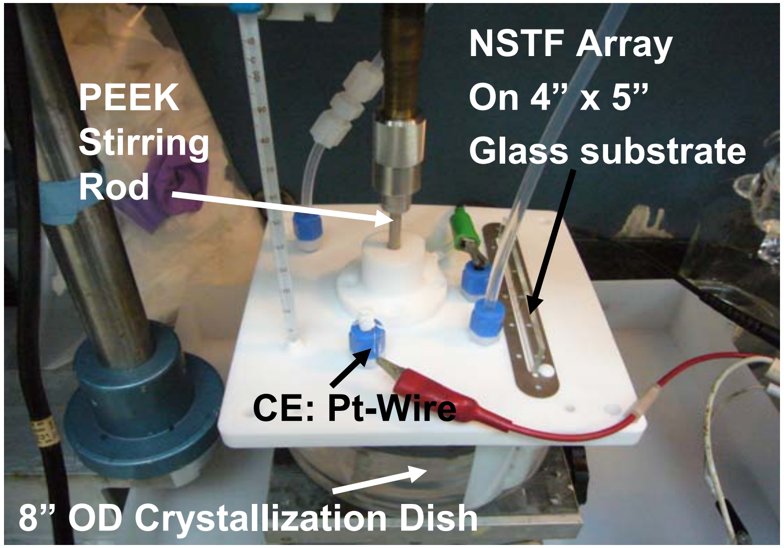
Status

- New NSTF ternary alloy fabricated on 4-electrode array of NSTF whiskers.
- Electrochemical performance measured in new cell
- NSTF Pt-A-B / Pt ECSA ratio of 14/8 obtained
- Observed highly linear Tafel slope over >2.5 decades

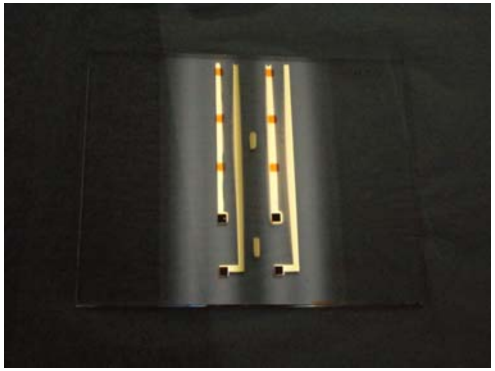
Tafel Plot for Pt-A-B NSTF



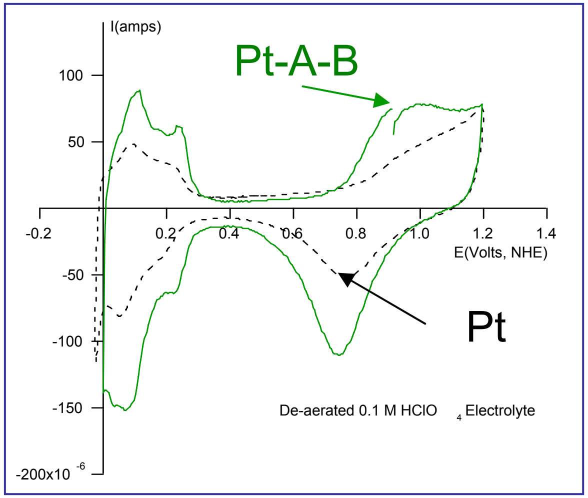
Electrochemical Cell Detailed View



4-electrode Pt-NSTF



CV Plot for Pt-A-B vs Pt

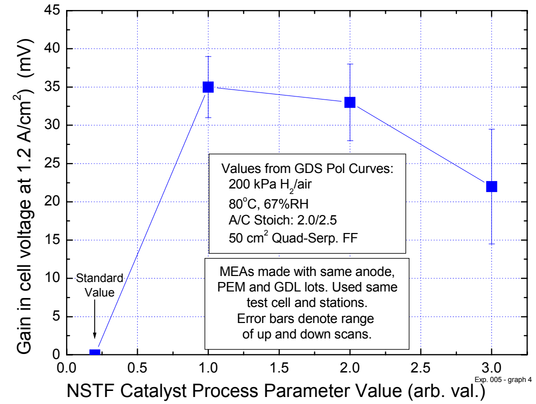


Technical Accomplishments: NSTF Catalyst Process Parameters

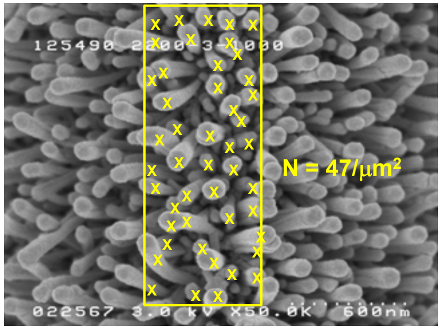
3M

Improved Pt catalyst deposition parameters:

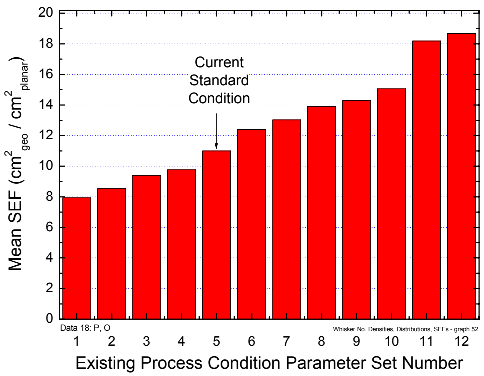
- 35-40 mV increase at 1.2 and 1.6 A/cm^2 over standard value
- 30% increase in A/cm^2 at 0.82V (iR-corrected)
- No statistically significant change in specific activity, mass activity, impedance or electrochemical surface area
- => Mass transfer over-potential reduced

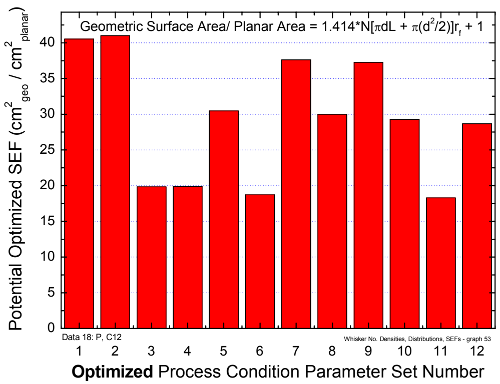


Catalyst support surface area optimization for mass activity:



- First designed experiment to optimize whisker support geometric area: *variable number density and lengths*
- Whiskers fabricated with 24 process condition parameter sets
- Physical statistical characteristics determined by SEM:
  - Extract areal number density, length and width distributions.
  - Calculate material conversion fractions, geometric surface area enhancement factor (SEF) as a function of catalyst support growth parameters.
  - Project potential gain in support surface area for optimized process conditions:





=> potential for > 3x gain in NSTF surface area from optimized support whiskers.

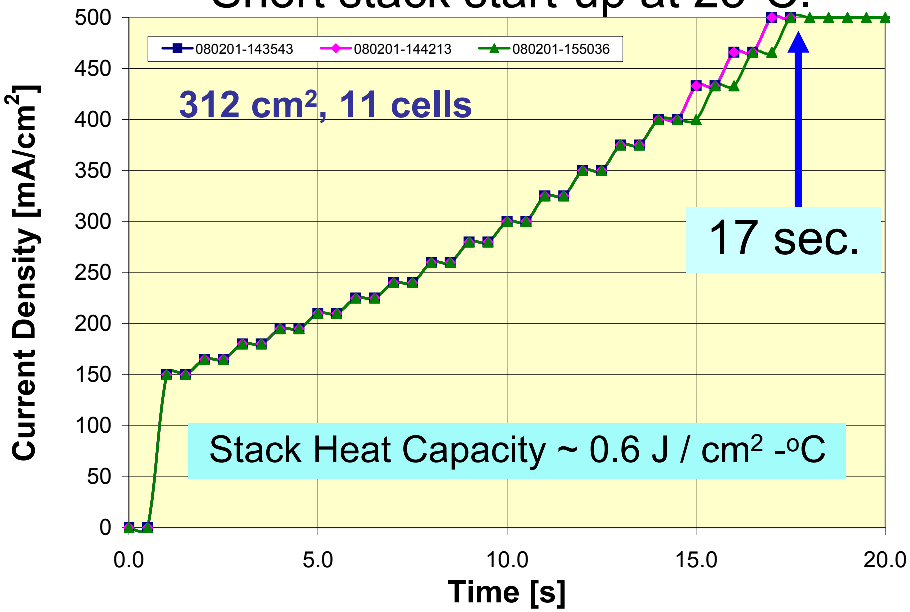
Technical Accomplishments: GDLs for NSTF Water Management

- Developed fuel cell test protocols for evaluating water management of ultra-thin electrodes under steady state and transient conditions.
- Demonstrated short-stack cool start capability vs. single cell.
- Demonstrated impact of reduced anode loading on water management
- Evaluated extensive material and process GDL factors for cool start

GDL Materials and Process Development

- Type of carbon paper electrode backing
- % and type of fluoropolymer used for wet proofing
- Drying conditions for wet proofing
- MPL coating weight and drying conditions
- GDLs without MPL
- Different GDLs for anode and cathode
- GDLs that covered gradient from completely hydrophilic to hydrophobic
- Three approaches for incorporation of hydrophilic materials into GDL
- Several types of proprietary processes
- Type and amount of fluoropolymer binder in MPL

Short stack start-up at 25°C.



Start-up from room temperature in a large-area stack is possible due to the transient nature of heat and water generation, and lower heat capacity than a single cell.

Future Work

Using $\leq$ 0.25 mg-Pt/cm^2 total per MEA:

Mass Activity Gain

- Continue to fabricate and test new catalyst compositions, structures and processes for a specific activity gain of 2x over current NSTF baseline without loss of durability under most severe accelerated test. Move best candidates to 50 cm^2 sized electrodes.
- Achieve $\geq$ 100% gain in catalyst surface area over current NSTF baseline without loss of specific activity or durability under most severe accelerated test. Complete evaluation of six independent approaches to increase surface area now in progress.

Durability Improvement

- Reduce by at least 50% any losses in surface area, activity or mass transport over-potential under the current most severe accelerated test protocol [fast high voltage (> 1 V) cycling]. Complete evaluation of two independent approaches in progress.
- Continue to explore limits of improvement for anode cell reversal tolerance with NSTFC.

Water Management Improvement

- Optimize the GDL materials and process conditions for more effective liquid water transport at low temperatures without compromising high temperature performance under dry conditions. Tailor the GDL for both anode and cathode independently to optimize performance over a wider range of operating conditions.
- Evaluate NSTF with improved membranes for enhanced performance under cold and wet or dry and hotter conditions.

Project Summary : Status Against Targets

Characteristic	Units	2010/2015 Targets	3M Status - Feb. 2008 (mfg'd roll-good)	Project Goal
PGM Total Content	g/kW rated in stack	0.3 / 0.2	**22 cell short stack:** 0.47 **50 cm² cell:** 0.27g/kW @ 0.62V, 150kPa inlet	**≤ 0.25 stack**
PGM Total Loading	mg PGM/cm² electrode area	0.3 / 0.2	**0.25** **(A/C = 0.1/0.15)**	**≤ 0.25**
Durability with Load Cycling At operating T ≤ 80°C At operating T > 80°C	Hours	 5000 / 5000 2000 / 5000	**7300 hours (still on test)** 50cm² cell, accelerated load cycling at 80/64/64°C	**> 5000**
Mass Activity (150kPa H_2/O_2 80°C. 100% RH)	A/mg-Pt @ 900 mV, 150kPa O_2	0.44 / 0.44	**0.18 – 0.25** (≤ 0.2 mg/cm²)	**> 0.5**
Specific Activity (150 kPa H_2/O_2 at 80°C, 100% RH)	μ A/cm²-Pt @ 900 mV	720 / 720	**2,900** (with 0.2 mg_{Pt}/cm²)	**> 5000**
Accel. Test loss, 30,000 cycles, 0.7 – 0.9V at 80°C	- mV at 0.8 A/cm² % ECSA loss	**< 30mV @ 0.8 A/cm²** < 40% / 40 %	**~ 0 mV loss at 0.8 A/cm²** **~ 0% loss ECSA**	**0** **0**
Accel. Test loss, 200 hrs @ 1.2 V at 95°C	- mV at 1.5 A/cm² % ECSA loss	< 30mV / 30mV < 40% / 40%	**+25mV gain at 1.5 A/cm²** **~17% loss ECSA**	**mV Gain** **0% loss**
Accel. Test loss, ~ 10,000 cycles 0.6-1.2V, 20mV/sec 90°C, 270kPa, H_2/N_2	% ECSA loss	??	**~ 30 % loss of ECSA**	**< 10% loss**

Project Summary: Overview

Relevance: Critically focused on overcoming the three most critical barriers for fuel cell MEA development.

Approach: Builds on 11 year DOE/3M funded development of NSTF catalyst and MEA technology that fundamentally has higher specific activity, removes all durability issues with carbon supports, much reduced losses due to Pt dissolution and membrane chemical attack, and has significant high volume manufacturing advantages.

Technical Accomplishments and Progress: Met or exceeded many of the specified DOE electrocatalyst/MEA performance and durability targets, clearly indicating the remaining gaps in mass activity and surface area stability under high voltage cycling. The project has identified multiple materials and process paths to meet or exceed these remaining targets.

Technology Transfer/Collaborations: Strong interactions with key partners has been very productive in identifying pathways to resolve the key gaps. New additional interactions with National Lab personnel should accelerate the progress and address other key issues.

Proposed Future Research: Strongly focused on the key remaining target gaps for mass activity, high voltage cycling stability, water management.